

FORM PTO-1390 (Modified) (REV 11-98)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>14283 (SIL 0034)</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN SEE 37 CFR 1.5) <b>09/806209</b>
INTERNATIONAL APPLICATION NO. <b>PCT/US99/22490</b>	INTERNATIONAL FILING DATE <b>27 September 1999 (27.09.99)</b>	PRIORITY DATE CLAIMED <b>28 September 1998 (28.09.98)</b>		
TITLE OF INVENTION <b>ORGANOSILOXANE CONTAINING MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS</b>				
APPLICANT(S) FOR DO/EO/US <b>George A. Policello, Anna Czech and Jack Burgazl</b>				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li> <li><input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> has been transmitted by the International Bureau.</li> <li>c. <input checked="" type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ul> </li> <li><input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li> <li><input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made.</li> </ul> </li> <li><input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li><input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li><input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> </ol>				
Items 13 to 20 below concern document(s) or information included:				
<ol style="list-style-type: none"> <li><input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input checked="" type="checkbox"/> Certificate of Mailing by Express Mail</li> <li><input checked="" type="checkbox"/> Other items or information:</li> </ol>				
<p><b>Courtesy copy of International Application</b></p> <p><b>Assignee: Crompton Corporation</b>  <b>Assignee Address: Middlebury, CT 06749</b></p>				

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) <b>09/806209</b>	INTERNATIONAL APPLICATION NO. <b>PCTUS99\22490</b>	ATTORNEY'S DOCKET NUMBER <b>14283 (SIL 0034)</b>																			
21. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>																			
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b>																					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1,000.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$860.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$690.00</b> <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b>																					
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$860.00</b>																			
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		<input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 <b>\$130.00</b>																			
<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 25%;">CLAIMS</th> <th style="width: 25%;">NUMBER FILED</th> <th style="width: 25%;">NUMBER EXTRA</th> <th style="width: 25%;">RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>10 - 20 =</td> <td>0</td> <td>x \$18.00      <b>\$0.00</b></td> </tr> <tr> <td>Independent claims</td> <td>3 - 3 =</td> <td>0</td> <td>x \$80.00      <b>\$0.00</b></td> </tr> <tr> <td colspan="2">Multiple Dependent Claims (check if applicable).</td> <td style="text-align: center;"><input type="checkbox"/></td> <td style="text-align: center;"><b>\$0.00</b></td> </tr> <tr> <td colspan="2" style="text-align: center;"><b>TOTAL OF ABOVE CALCULATIONS =</b></td> <td style="text-align: center;"><b>\$990.00</b></td> </tr> </tbody> </table>		CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	10 - 20 =	0	x \$18.00 <b>\$0.00</b>	Independent claims	3 - 3 =	0	x \$80.00 <b>\$0.00</b>	Multiple Dependent Claims (check if applicable).		<input type="checkbox"/>	<b>\$0.00</b>	<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$990.00</b>	
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/> <b>\$0.00</b>																			
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<p><input type="checkbox"/> A check in the amount of _____ to cover the above fees is enclosed.</p> <p><input checked="" type="checkbox"/> Please charge my Deposit Account No. <b>23-2656</b> in the amount of <b>\$990.00</b> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p><input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. <b>23-2656</b> A duplicate copy of this sheet is enclosed.</p>																					
<p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b></p> <p>SEND ALL CORRESPONDENCE TO:</p> <p>Edward W. Grolz SCULLY, SCOTT, MURPHY &amp; PRESSER 400 GARDEN CITY PLAZA GARDEN CITY, NEW YORK 11530 (516) 742-4343</p>																					
 <b>SIGNATURE</b>																					
<b>Edward W. Grolz</b> <hr/> <b>NAME</b> <hr/> <b>33,705</b> <hr/> <b>REGISTRATION NUMBER</b> <hr/> <b>March 27, 2001</b> <hr/> <b>DATE</b>																					

09/806209

## CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)

JC03 Rec'd PCT/US 3 MAR 2001

Applicant(s): George A. Policello, Anna Czech and Jack Burgazl

14283

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Filing Date

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Invention: ORGANOSILOXANE CONTAINING MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS

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## Organosiloxane Containing Modified Groups in Pesticidal Compositions

### **Background of the Invention**

Many pesticides require the addition of an adjuvant to the spray mixture to provide wetting and spreading on foliar surfaces. Often that adjuvant is a surfactant, which can perform a variety of functions, such as increasing spray droplet retention on difficult to wet leaf surfaces, or to provide penetration of the herbicide into the plant cuticle. These adjuvants are provided either as a tankside additive or used as a component in pesticide formulations.

Gaskin, *et al.*, (*Pestic. Sci.* 1993, **38**, 185-192) demonstrated that some trisiloxane ethoxylates (TSE), such as Silwet L-77<sup>®</sup> surfactant (available from Witco Corp. of Greenwich, CT), can antagonize cuticular penetration of a herbicide into grasses, when compared to the herbicide alone. The term antagonism is used to indicate that the treatment of herbicide plus adjuvant is less effective than the comparative herbicide treatment.

Sandbrink, *et al.*, (*Pest. Sci.* 1993, **38**, 272-273) published that a TSE antagonized glyphosate performance relative to glyphosate alone in the control of *Panicum maximum* Jacq. Snow, *et. al.*, Langmuir, 1993, **9**, 424-30, discusses the physical properties and synthesis of novel cationic siloxane surfactants. These siloxanes are based on the reaction of a chloropropyl modified trisiloxane with an alkanolamine, such as N-methylethanolamine, which was further reacted with a halide to make a quaternary surfactant.

Petroff, *et al.*, (EP 92116658) describes the use of cationic, quaternary trisiloxanes to enhance the efficacy of glyphosate on velvetleaf, a broadleaf weed. Henning, *et al.*, (DE4318537) describes cationic siloxanyl modified polyhydroxy hydrocarbon or carbohydrate for use with plant protection agents. These 5 compounds are derived from a saccharide containing 1 to 10 pentose and/or hexose units, modified with a quaternary ammonium group, and a siloxane moiety. Reid, *et al.*, (USP 3,389,160) describes amino modified siloxane alkoxylates where the amino functionality appears as the terminal group on the alkyleneoxide moiety, opposite the siloxane group. Policello in PCT WO 10 97/32475 discloses amino modified siloxanes wherein the amine is bound by an ether bond to the siloxane backbone wherein the amine may be terminal or pendant to the backbone.

Dietz et al. in US Patent No. 5,891,977 describes organopolysiloxanes comprising polyhydroxyorganyl radicals and polyalkylene radicals, their process 15 and use. Specifically these materials are described as being useful in coatings, paints and inks, as well as emulsifiers for water-in-oil and oil-in-water systems, such as hair care formulations. Although these materials are mentioned as being practical for many applications, these were not shown to have utility as adjuvants for pesticidal applications.

20

### **Summary of the Invention**

Organosiloxanes for use with pesticidally active compositions and those with utility in pesticide formulations to treat plants and animals are those

substituted with at least one aminealkoxylate group, which are novel siloxane structures. Intermediates for the manufacture for said siloxane are also disclosed herein.

## 5    Detailed Description of the Invention

The amino alkoxylate organosiloxanes described herein are useful as adjuvants for pesticide formulations, including but not limited to applications which may be used to treat plants or animals. The pesticidal formulations include (a) at least one modified organosiloxane; and (b) at least one pesticidally active component, but may contain optional ingredients.

### (A) ORGANOSILOXANES

Preferably, the modified organosiloxanes of the present invention have the average general formula:



wherein f is between 0 to 50, preferably 1 to 5, more preferably 1 to 2, most preferably 1, d = 0 to 2, most preferably 0, e = 0 to 3, most preferably 0, if the siloxane is not cyclic, g = 2 + e + 2d, and if the siloxane is cyclic g = 0 and f  $\geq$  1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic 20 and Q is either an amino alkoxylate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, preferably 2 to 3, each b is 2 to 15, preferably 2 to 8, each B is a divalent bridging group of C1 to C8, preferably C3 to C4, each optionally OH substituted, z = 0 to 1, preferably 0, R<sup>1</sup> is

hydrogen or a hydrocarbon radical of 1 to 4 carbons, R<sup>2</sup> is either a polyether of the structure -BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>c</sub>R<sup>1</sup>, hydrogen, an alkyl radical containing 1 to 18 carbons, preferably methyl, c is 0 to 15, and T is a univalent organic moiety.

Preferably most R<sup>2</sup> groups are methyl, but some may be polyethers of the  
5 structure -B(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup> as defined above, e.g., -C<sub>3</sub>H<sub>6</sub>(C<sub>2</sub>H<sub>4</sub>O)<sub>8</sub>OH and  
-C<sub>3</sub>H<sub>6</sub>(C<sub>2</sub>H<sub>4</sub>O)<sub>6</sub>(C<sub>3</sub>H<sub>6</sub>O)<sub>2</sub>OCH<sub>3</sub>. Exemplary B are -(CH<sub>2</sub>)<sub>2</sub>-, -(CH<sub>2</sub>)<sub>3</sub>-, and  
-CH<sub>2</sub>CH(OH)CH<sub>2</sub>- and -CH<sub>2</sub>C<sub>6</sub>H<sub>9</sub>(OH)CH<sub>2</sub>- Examples of R<sup>1</sup> are -H, and -CH<sub>3</sub>.  
Most preferably all Q groups which are terminal are methyl and there is at least  
one amino alkoxylate pendant, though alternatively, the terminal groups may be  
10 amino alkoxylates and the pendant Q groups may all be methyl. A particularly  
preferred siloxane is a (CH<sub>3</sub>)<sub>3</sub>SiOSiCH<sub>3</sub>(Q)OSi(CH<sub>3</sub>)<sub>3</sub> wherein the Q is an amino  
alkoxylate.

Preferably a is such that there is a mixture of ethylene oxide (EO),  
propylene oxide (PO) units and butylene oxide (BO) units. Preferably, for  
15 aqueous applications, there is a preponderance of EO units, most preferably  
every a = 2. For non-aqueous applications, such as crop oil concentrates, there  
may be more PO and BO units. When Q contains a mixture of oxyalkylenes, it  
may be blocked or random. One skilled in the art will understand the  
advantages in the position of the oxyethylene relative to the oxypropylene, when  
20 the alkyleneoxide group is blocked.

T groups preferably are alkyls (which may be branched, linear or cyclic) of  
less than 8 carbons. Another preferred T is an alkyl amine functionality, -BNR<sup>2</sup>,  
which may be further substituted (e.g., with an alkyl) or be further alkoxylated,

e.g.,  $-\text{BN}(\text{C}_a\text{H}_{2a}\text{O})_c\text{R}^1$ . Alternatively, T may be an amino alkyl siloxane or an amino alkyl hydroxy siloxane, e.g.,  $-\text{B-N-B-(SiO}_{1/2}\text{R}^6\text{-X}^1$  wherein  $\text{X}^1$  is a siloxane per formula I above (with the  $-\text{B-N-B-(SiO}_{1/2}\text{R}^6\text{-X}^1$  group being taken as  $[\text{O}_{1/2}\text{MeSi(Q)O}_{1/2}]$  or  $[\text{O}_{1/2}\text{SiMe}_2\text{Q}]$ ) and  $\text{R}^6$  is  $\text{O}_{1/2}$  or  $-\text{CH}_3$ . If T contains a siloxane, it 5 preferably is the same backbone as the siloxane to which Q is attached.

The Q groups may include protonated amines, i.e., where there is a hydrogen ion attached to the nitrogen in the Q group, which can occur to the aminosilicone alkoxylates under acidic conditions. Also contemplated herein are quaternary versions of Q, i.e., where there is a third T group on the nitrogen in 10 Q, but said quaternary compounds are not preferred for use in the present invention since they would tend to be phytotoxic.

Preferred Q structures are wherein  $\text{R}^4$  is hydrogen or methyl, a is 2, and b is from 4 to 6. Specific Q groups are  $-\text{C}_2\text{H}_4\text{N}[\text{C}_2\text{H}_4\text{O(EO)}_5\text{CH}_3]_2$ ;  $-\text{C}_2\text{H}_4\text{N}[\text{C}_2\text{H}_4\text{O(EO)}_6\text{H}]_2$ ;  $-\text{C}_3\text{H}_6\text{N}[\text{C}_3\text{H}_6\text{O(EO)}_3(\text{PO})_2\text{H}](\text{C}_2\text{H}_5)$ ; 15  $-\text{C}_3\text{H}_6\text{OCH}_2\text{CH(OH)CH}_2\text{N}[\text{C}_2\text{H}_4\text{O(EO)}_6\text{H}]_2$ ;  $-\text{C}_3\text{H}_6\text{OCH}_2\text{CH(OH)CH}_2\text{NH}[\text{C}_3\text{H}_6\text{O(EO)}_6\text{H}]$ ;  $-\text{C}_3\text{H}_6\text{C}(\text{CH}_3)_2\text{N}(\text{C}_2\text{H}_5)[\text{C}_3\text{H}_6\text{O(PO)}_5\text{H}]$ ;  $-\text{C}_3\text{H}_6\text{OCH}_2(\text{OH})\text{CH}_2\text{NHC}_3\text{H}_6\text{O(EO)}_2\text{CH}_2\text{CH(CH}_3\text{)NHCH}_2\text{CH(OH)CH}_2\text{OC}_3\text{H}_6\text{SiO}_{22}((\text{CH}_3)_3\text{SiO}_{1/2})_2$ ; and  $-\text{C}_3\text{H}_6\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{CH}_2\text{CH(OH)CH}_2\text{N}[\text{CH}_2\text{CH}_2\text{O(EO)}_4\text{H}]_2$ .

Preferred aminosilicone alkoxylates are trisiloxanes with  $\text{R}^5$  being methyl, with 20 B preferably being a C1 to C4 alkylene, most preferably propylene or 2-hydroxy propylene.

PESTICIDES

The pesticidal compositions of the present invention also include at least one pesticide, especially acid functionalized ones, i.e., compounds that contain at least one carboxylic, sulfonic or phosphonic acid group or their salt or ester. The term pesticide means any compound used to destroy pests, e.g., rodenticides, fungicides, and herbicides. Illustrative examples of pesticides which can be employed include, but are not limited to, growth regulators, photosynthesis inhibitors, pigment inhibitors, mitotic disrupters, lipid biosynthesis inhibitors, cell wall inhibitors, and cell membrane disrupters. The amount of pesticide employed in compositions of the invention varies with the type of pesticide employed. More specific examples of pesticide compounds that can be used with the compositions of the invention are: phenoxy acetic acids, phenoxy propionic acids, phenoxy butyric acids, benzoic acids, triazines and s-triazines, substituted ureas, uracils, bentazon, desmedipham, methazole, phenmedipham, pyridate, amitrole, clomazone, fluridone, norflurazone, dinitroanilines, isopropalin, oryzalin, pendimethalin, prodiamine, trifluralin, glyphosate, sulfonylureas, imidazolinones, clethodim, diclofop-methyl, fenoxaprop-ethyl, fluazifop-p-butyl, haloxyfop-methyl, quizalofop, sethoxydim, dichlobenil, isoxaben, and bipyridylium compounds.

The pesticide may be a liquid or a solid. If a solid, it is preferable that it is soluble in a solvent prior to application, and the silicone may act as a surfactant for such solubility or additional surfactants may perform this function.

It is preferable that the pesticide be one that is other than a solvent. For example, it is preferable that the pesticide do not include solvents which have also at times been categorized as being pesticidally active compounds. Such solvents include paraffinics; oils including animal, mineral, vegetable, silicone, 5 and so forth; fatty acids, esters, and amides of fatty acids; alkanes; ketones; alcohols; glycols; alkyl/aryl alkoxylates; diols; acetates; and so forth.

### EXCIPIENTS

Buffers, preservatives and other standard excipients known in the art also 10 may be included in the composition. When the compositions of the present are insoluble in distilled water, spreading may be achieved by the addition of a small amount of an acid, such as acetic acid, to protonate the amine functionality, thereby increasing water solubility.

Solvents may also be included in compositions of the present invention. 15 These solvents are in a liquid state at room temperature. Examples include water, alcohols, aromatic solvents, oils (i.e. mineral oil, vegetable oil, silicone oil, and so forth), lower alkyl esters of vegetable oils, fatty acids, ketones, glycols, polyethylene glycols, diols, paraffinics, and so forth. Particular solvents would be 2, 2, 4-trimethyl, 1-3-pentane diol and alkoxylated (especially ethoxylated) 20 versions thereof, See US Patent No. 5,674,832 to Keyes, or n-methyl-pyrrilidone.

Moreover, other cosurfactants, which have short chain hydrophobes which do not interfere with superspreading may be included. See US Patent No. 5,558,806 to Policello et al., which is incorporated by reference.

- The cosurfactants useful herein include nonionic, cationic, anionic,  
5 amphoteric, zwitterionic, polymeric surfactants, or any mixture thereof.

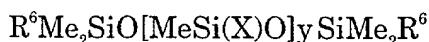
Surfactants are typically hydrocarbon based, silicone based or fluorocarbon based.

Useful surfactants include alkoxylates, especially ethoxylates, containing block copolymers including copolymers of ethylene oxide, propylene oxide,  
10 butylene oxide, and mixtures thereof; alkylaryllalkoxylates, especially ethoxylates or propoxylates and their derivatives including alkyl phenol ethoxylate; arylarylalkoxylates, especially ethoxylates or propoxylates. and their derivatives; amine alkoxylates, especially amine ethoxylates; fatty acid alkoxylates; fatty alcohol alkoxylates; alkyl sulfonates; alkyl benzene and alkyl  
15 naphthalene sulfonates; sulfated fatty alcohols, amines or acid amides; acid esters of sodium isethionate; esters of sodium sulfosuccinate; sulfated or sulfonated fatty acid esters; petroleum sulfonates; N-acyl sarcosinates; alkyl polyglycosides; alkyl ethoxylated amines; and so forth.

Specific examples include alkyl acetylenic diols (SURFONYL-Air Products), pyrrolidone based surfactants (e.g., SURFADONE - LP 100 - ISP), 2-ethyl hexyl sulfate, isodecyl alcohol ethoxylates (e.g., RHODASURF DA 530 - Rhodia), ethylene diamine alkoxylates (TETRONICS - BASF), and ethylene

oxide/propylene oxide copolymers (PLURONICS – BASF) and Gemini type surfactants (Rhodia).

Preferred surfactants include ethylene oxide/propylene oxide copolymers (EO/PO); amine ethoxylates; sorbitol ethoxylates; and so forth. The optional 5 silicone surfactants include trisiloxane alkoxylates (TSAs) of the general formula:



wherein y = 0 to 2, preferably 1, X is as above, and R<sup>6</sup> is G, or an alkyl of one to four carbons. The preferred nonionic siloxane alkoxylates are trisiloxane 10 alkoxylates, where y = 1, a = 3, q = 4 to 8, r = 0, R<sup>6</sup> is Me, R<sup>3</sup> is H or Me.

A suspension aid is preferably utilized if a pesticide concentrates is made with the modified siloxanes to improve physical stability.

#### MANUFACTURE OF SILOXANES

15 The amine modified organosiloxanes of the present invention may be made by the hydrosilation of a hydridosiloxane with an epoxy intermediate, such as allyl glycidal ether, vinyl cyclohexene monoxide, or an epoxy terminated allyl polyalkyleneoxide, followed by ring opening the epoxide with the appropriate amino alkoxylate group. The hydridosiloxanes described are commercially 20 available and may be made as known in the art. Hydrosilation conditions depend on the reactants, but are within the general conditions taught in Marciniec (*Comprehensive Handbook of Hydrosilylation*, Edited by Bogdan Marciniec, Pergamon Press).

Epoxy terminated, allyl polyethyleneoxide can be prepared by the method outlined by Xue-Ping Gu, *et al.*, (Synthesis of Glycol Diglycidyl Ethers Using Phase-Transfer Catalysis; in *Synthesis Communications June/July 1985*, p. 649-651) from an epoxide and commercially available allyl started polyalkylene oxides.

Amino alkoxylates which are to be reacted with the epoxide may be terminated with an alkyl or hydroxyl or may be terminated with an amine, so that the alkoxylate is a diamine. Such diamines are available under the tradename JEFFAMINE. In such a case the diamine would crosslink many of the siloxanes, thus, it is preferable to use with diamines siloxanes with only one epoxy functionality per molecule. The resulting product would be two siloxane chains linked by an amino alkoxylate amino bridge. Short chain siloxanes, e.g., trisiloxanes would be preferable for same.

Alternatively to make the amine modified siloxanes one may start from the reaction product of an allyl or methallyl chloride and an alkoxylated amine compound and hydrosilate this allylic polyhydric amine onto hydridosiloxanes. Hydrosilation conditions depend on the amine and siloxane, but again are within the general conditions taught in Marciniec.

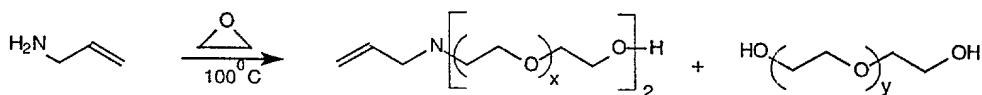
If a siloxane is a terpolymer, i.e., has two different functionalities hydrosilated onto the backbone (e.g., an amino alkoxylate, polyether siloxane) such hydrosilations may be done sequentially or at the same time depending upon the reactivities of the species to be hydrosilated, as well as the desired end-

product. The reaction conditions for hydrosilating an allyl started polyether are well known in the art.

The alkenylamino polyalkyleneoxides intermediate structures to be reacted with the hydridosiloxanes are of the formula  $B'N[BO(C_aH_{2a}O)_bR']_{2-z}T_z$  5 wherein all formulae as are above, except B' is an alkenyl, with an  $\alpha$ ,  $\beta$  unsaturation at the end of the alkenyl opposite from the nitrogen atom. The alkenyl could be C1-C18, preferably C1-C6, and most preferably allyl or methallyl. To make this alkenyl amine alkoxylate, an alkenyl salt, e.g., allyl bromide, is reacted with ammonia, or a secondary or primary amine. This amine 10 product then is alkoxylated.

An exemplary alkoxylation procedure would be as follows (with chemistry noted below)- Charge allyl amine to reactor. Degas and pressurize with nitrogen. Heat to 105°C, and then add 25 psig (.0015 N<sup>2</sup>/m) of nitrogen above the pressure exerted by allyl amine. Gradually add EO, to maintain temperature 15 below 115 C, and pressure below 80 psig (.0095 N<sup>2</sup>/m). The formation of the tertiary amine will cause a great drop in the reactor pressure, at this time continual addition of EO could proceed at 105-110°C and a pressure range of 60 - 80 psig (0.0066 to 0.0095 N<sup>2</sup>/m). After the required amounts of EO is added, the reaction is allowed to digest for 30 minutes, residual EO is removed by vacuum, 20 the reactor is cooled, and the product removed by slight pressurization of the reactor.

Any glycol's which may have been produced due to utilization of a partially wet amine may be stripped by vacuum.



The allyl amino polyalkyleneoxides also may be prepared by reaction of an allyl glycidyl ether (or similar unsaturated epoxide) with an amine alkoxylate (which result in an ether bond). If a diamine is used for such a reaction, a 5 diallylic species will be formed, which will act as a crosslinker and preferably should be used with a mon-hydridosiloxane. An alternative method uses aziridine, which is not preferred for toxicity reasons, are disclosed in PCT US97/04128, which is incorporated herein by reference.

The nonionic siloxane and the pesticides are commercially available and 10 their manufacture is known in the art.

### USE

The modified organosiloxanes may be used in agricultural applications as adjuvants for pesticides wherein the siloxane is applied in a pesticide 15 formulation to agricultural products or to treat animals. The composition of the present invention is useful as a tank side additive in an animal shampoo, or as a component in a herbicide formulation. In addition the compositions of the present invention are useful as adjuvants for other pesticides, such as, fungicides, insecticides, plant growth regulators, acaracides and the like. The 20 pesticide formulations may be wet, dry, slurries or other formulations as are known in the art.

The siloxanes are added directly to a spray tank along with an acid functional pesticide, or as part of a pesticide formulation. When used as a tankside additive, the siloxane is present at weight concentrations between 0.001% and 5.0%, preferably between 0.025% and 0.5%. Likewise, when the 5 modified organosiloxanes are used in a pesticide formulation (In-can), they are present at weight concentrations that will deliver between 0.001% and 5.0% to the final use dilution, preferably between 0.025% and 0.5%, of the final use dilution.

It is noted that most dilutions will be made with water, but in the case of 10 crop oil concentrates, oils (mineral, silicone, animal or vegetable oils) will be the diluents.

When the compositions of the present invention are used in conjunction with a TSA, the weight ratio of the TSA to the modified organosiloxanes is between 5:95 and 95:5, preferably between 5:95 and 40:60. The blend may be 15 accomplished by mixing physically the two components prior to use, or by adding them separately to a spray mixture at the point of use.

When the compositions of the present invention are used in conjunction with nonsilicone surfactants, the weight ratio of the nonsilicone surfactant to the modified organosiloxane is between 1:99 and 99:1, preferably between 99:1 and 20 40:60.

Additionally, the amino alkoxylate organosiloxanes also may be used generally as surface active agents in aqueous formulation where there is an acid functionalized component. These organosiloxanes also may be used as surface

active agents, including, but not limited to, as surfactants, wetting agents and softeners for textiles, flow and leveling agents in coatings, hair care products, skin care and creams for personal care applications and anti-static agents, detergents and softeners for laundry products.

5

### Examples

Unless otherwise indicated, all parts and percentages are by weight, and are based on the weight at the particular stage of the processing being described.

#### Example 1 - Alkoxylation of Allyl Amine

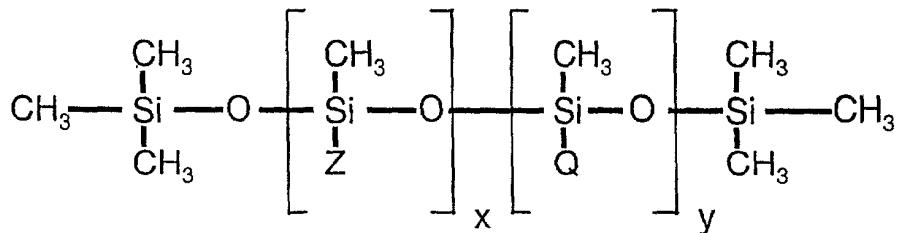
To a two liter Parr pressure reactor was charged 200.4 g of allyl mine. The reactor was heated to 60°C, which resulted in a pressure of 10 psig. To the system was added 25 psig of nitrogen, and 50 g of EO. The reactor was heated  
10 gradually until an exotherm was noticed. This occurred at 103°C and caused a pressure jump to 105 psig. After the reaction subsided the temperature was kept at 103 and more EO added between 40 - 60 psig. After approximately 100 g was added another exotherm occurred to 130°C and caused a raise in pressure to 70 psig. After this exotherm subsided the reaction behaved very well and  
15 continuous addition of EO was possible. Catalysis after the formation of a tertiary amine was not required for subsequent addition of EO. The temperature range of the reaction was 103 -110°C, with a pressure of range of 40 - 45 psig (including 25 psi of Nitrogen), and a rate of addition of 20-25 g/min. of EO.

Example 2

Aminosilicone alkoxylates were prepared by the slow addition of the desired allylamino polyalkyleneoxide to a reaction vessel containing heptamethyltrisiloxane (in a 1.3:1 mole ratio). Therefore, 25.7g of 5 heptamethyltrisiloxane (0.1155 moles), 39.3g of allylamine ethoxylate, 4.6 EO, (0.1501 moles), along with 30 g isopropanol (solvent) were weighed into a 250 mL roundbottom flask equipped with an addition funnel, reflux condenser and an overhead stirrer. The flask contents were heated to 65°C and catalyzed with 0.3 g of potassium trichloro-ethylene platinate (III) solution (1% in isopropanol) and 10 held at this temperature for 6 h. The reaction mixture was heated to 75 °C , and an additional 0.56 g of catalyst solution was added. The reaction mixture was maintained at this temperature for an additional 5 hours at which time another 0.26 g of catalyst solution was added to the reaction mixture, and stirred for an additional hour. The reaction was monitored by introducing a sample of the 15 reaction mixture into a fermentation tube containing KOH/water/ethanol solution. The generation of hydrogen indicates an incomplete reaction. The flask contents were mixed until the SiH intermediate was consumed. The mixture was cooled to 45 °C, filtered through a fine filter pad, and stripped on a Rotovap for 1.5 hours at 70°C and 1.0 mm Hg to yield a dark amber colored 20 product with a viscosity of 78 cps (Spindle LV-3 @ 100 rpm), a refractive index of 1.4520 (25°C) and an aqueous surface tension of 21.1 mN/m (0.1 wt%, Wilhelmy Plate). The resulting aminosilicone alkoxylate is shown in Table 1.

Table 1

## Description of Modified Organosiloxanes



5

Reference	<u>x</u>	<u>y</u>	Description
MSIL-1	0	1	$Q = C_2H_4N[(C_2H_4O)_aH_3]_2$ , where $a = 4.6$

## Example 3

10 This example demonstrates the utility of the organosilicone composition of the present invention as a surfactant. Aqueous solutions of this siloxane provided a significant reduction in surface tension relative to water. Surface tension was measured using a Cahn microbalance, with a sand blasted platinum blade as the sensor. Solutions of the various components were prepared at 0.1  
 15 wt% in 0.005M NaCl water (Deionized), as an equilibrium aid.

Spreading was determined by applying a 10  $\mu\text{L}$  droplet of surfactant solution to a polyester film (3M, IR 1140 transparency film) and measuring the spread diameter after 30 seconds. The solution was applied with an automatic pipette to provide droplets of reproducible volume. Deionized water that was

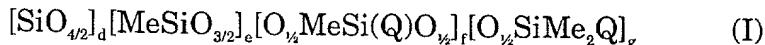
further purified with a Millipore filtration system was used to prepare the surfactant solutions.

**Table 2 - Comparison of Aqueous Surface Tension Properties**

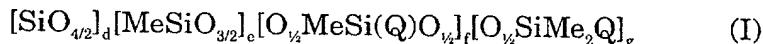
<u>Surfactant</u>	<u>Surface Tension (mN/m)</u>	<u>Spread Diameter (mm)</u>	
		<u>0.1 wt%</u>	<u>0.2 wt%</u>
MSIL-1	21.1	27	34
a. Surface tension in mN/m at 25°C.			
b. Surface tension of water from <u>CRC Handbook of Chemistry and Physics</u> ; 63 Edition, 1982-1983.			
* Spread diameter of distilled water = 4 mm			

We claim:

1. A modified organosiloxanes of the present invention have the average general formula:



- 5 wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an amino alkoxylate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging
- 10 group of C1 to C8, each optionally OH substituted, z = 0 to 1, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R<sup>2</sup> is either a polyether of the structure -BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>c</sub>R<sup>1</sup>, hydrogen or an alkyl radical containing 1 to 18 carbons, c = 0 to 15, and T is a univalent organic moiety.
2. A composition according to claim 1 wherein T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, -BNR<sup>1</sup><sub>2</sub>, or B-N-B-(SiO<sub>1/2</sub>R<sup>6</sup>)-X<sup>1</sup> wherein X<sup>1</sup> is a siloxane per formula I and R<sup>6</sup> is O<sub>1/2</sub> or -CH<sub>3</sub>.
- 15 3. A composition according to claim 1 wherein f = 1 to 5, d = 0, e = 0 and g = 2.
- 20 4. A composition according to claim 1 additionally comprising a pesticide.
5. A composition according to claim 3 wherein T is an alkyl and z = 1.
6. A process for applying a pesticide comprising applying to an animal or plant a composition comprising:



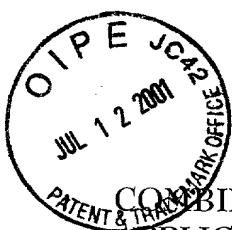
wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic, g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an  
 5 amino alkoxylate of the formula -BN[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> or R<sup>2</sup>, with at least one Q not being R<sup>2</sup>, each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging group of C1 to C8, each optionally OH substituted, z = 0 to 1, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R<sup>2</sup> is either a polyether of the structure -BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>, hydrogen or an alkyl radical containing 1 to 18 carbons and T is  
 10 a univalent organic moiety.

7. A process according to claim 6 additionally comprising applying a cosurfactant.

8. A process according to claim 6 wherein f = 1 to 5, d = 0, e = 0 and g = 2 and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an  
 15 alkyl amine functionality, -BNR<sup>1</sup><sub>2</sub>, or B-N-B-(SiO<sub>1/2</sub>R<sup>6</sup>)-X<sup>1</sup> wherein X<sup>1</sup> is a siloxane per formula I and R<sup>6</sup> is O<sub>1/2</sub> or -CH<sub>3</sub>.

9. An amine of the formula B'N[BO(C<sub>a</sub>H<sub>2a</sub>O)<sub>b</sub>R<sup>1</sup>]<sub>2-z</sub>T<sub>z</sub> wherein B' is an alkenyl, with an α, β unsaturation at the end of the alkenyl opposite from the nitrogen atom, a = 2 to 4, b = 2 to 15, z = 1 to 2, B is a divalent bridging group of C1 to C8, each optionally OH substituted, R<sup>1</sup> is hydrogen or a hydrocarbon radical of 1 to 4 carbons and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, or -BNR<sup>1</sup><sub>2</sub>.

10. An amine according to claim 9 wherein z = 0.



## COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Includes Reference to PCT International  
Applications)

Atty Docket No. SIL-0034 (14283)  
Page 1 of 4

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the invention entitled:

### "ORGANOSILOXANE CONTAINING MODIFIED GROUPS IN PESTICIDAL COMPOSITIONS"

which is described and claimed in the patent specification which

( ) is attached hereto,

was filed on September 28, 1999 and accorded serial number 09/806,209, and for which  
invention Letters Patent are sought.

I hereby state that I have reviewed and understand the contents of the above identified  
specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this  
application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any  
foreign application(s) for patent or inventor's certificate listed below and have also identified below any  
foreign application for patent or inventor's certificate having a filing date before that of the application  
on which priority is claimed:

PRIOR FOREIGN/PCT APPLICATIONS AND PRIORITY CLAIMS UNDER 35 U.S.C. 119			
COUNTRY (if PCT, indicate "pct")	APPLICATION NO.	DATE OF FILING (month,day,year)	PRIORITY CLAIMED

COMBINED DECLARATION FOR PATENT  
APPLICATION AND POWER OF ATTORNEY

Atty Docket No No. SIL-0034 (14283)  
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(Includes Reference to PCT International  
Applications)

I hereby claim the benefit under Title 35, United States Code, Sec.120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec.112, I acknowledge the duty to disclose material information as defined in Title 37, Code Federal Regulation Sec.1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120				
U.S. APPLICATIONS			STATUS (CHECK ONE)	
US APPLN. NO.	US FILING DATE		PATENTED	PENDING
60/102,039	September 28, 1998			X
PCT APPLICATIONS DESIGNATING THE U.S.				
PCT APPLICATION NO.	PCT FILING DATE	US SERIAL NOS. ASSIGNED (if any)		
PCT/US99/22490	Sept. 27, 1999	09/806,209		

I hereby appoint the following attorney's and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: Kenneth D. Tremain - Reg. No. 20,518; and Daniel Reitenbach - Reg. No. 30,970.

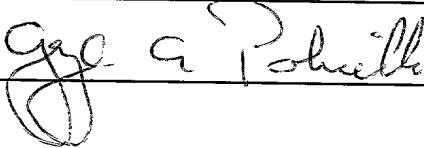
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

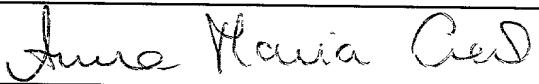
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Page 3 of 4

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(Includes Reference to PCT International  
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